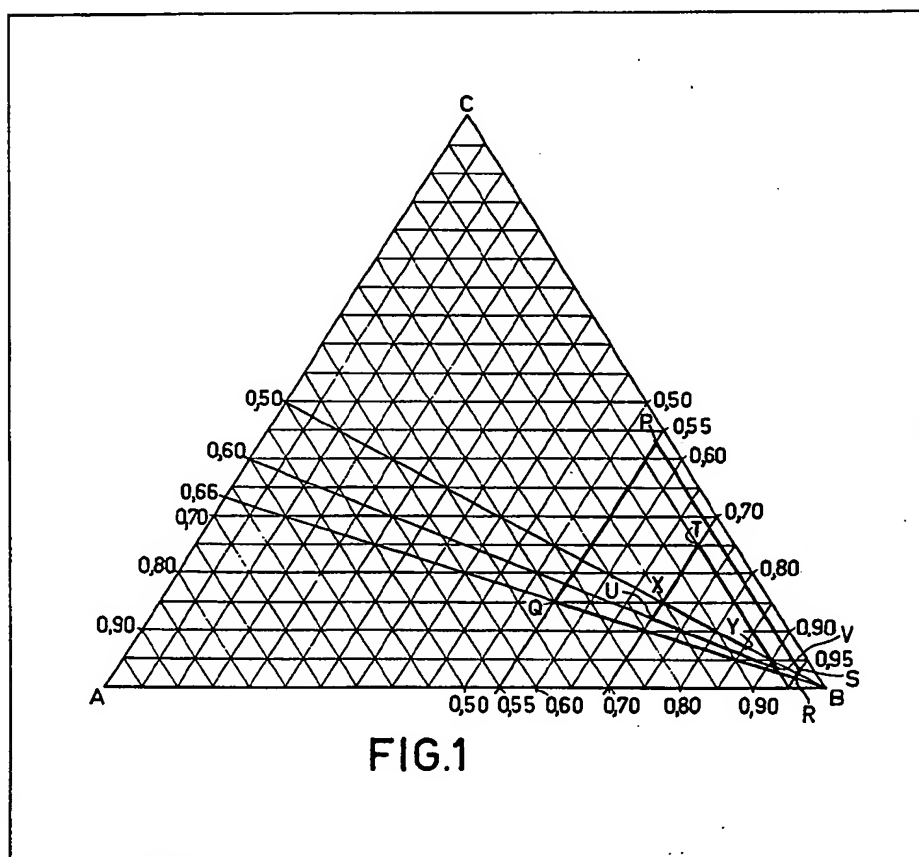


- (21) Application No 7939798
(22) Date of filing 16 Nov 1979
(30) Priority data
(31) 7811436
(32) 21 Nov 1978
(33) Netherlands (NL)
(43) Application published
13 Aug 1980
(51) INT CL³
C09K 11/30 11/46
(52) Domestic classification
C4S 311 43Y 703 70Y 712
713 714 71Y 720 721 724
725 730 750 751 757 758
75Y 764 765 766 782 78Y
(56) Documents cited
GB 2016034A
GB 1533507
(58) Field of search
C4S
(71) Applicants
N.V. Philips' Gloeilam-
penfabrieken
Emmasingel 29,
NL-5611 Eindhoven,
The Netherlands
(72) Inventors
Gert Marinus Boogerd,
Johannes Theodorus
Wilhelmus de Hair
(74) Agents
R.J. Boxall

(54) Luminescent materials

(57) Luminescent materials comprising luminescent ternary aluminates having a hexagonal crystal structure corresponding to the magnetoplumbite structure, which contain gadolinium and which are activated by at least one of the elements Pb, Sb, Ce, Sn, Tb, Mn, Cr, and Dy. The composition of the aluminate can be represented in a ternary phase diagram of a system ABC, wherein A represents $\frac{1}{2}\text{Gd}_2\text{O}_3$ and at least one of the oxides $\frac{1}{2}\text{La}_2\text{O}_3$, $\frac{1}{2}\text{Ce}_2\text{O}_3$, $\frac{1}{2}\text{Tb}_2\text{O}_3$, $\frac{1}{2}\text{Dy}_2\text{O}_3$, $\frac{1}{2}\text{Sb}_2\text{O}_3$, PbO, SnO, wherein at least 1 mol. % A is $\frac{1}{2}\text{Gd}_2\text{O}_3$, not more than 60 mol. % A is $\frac{1}{2}\text{Tb}_2\text{O}_3$, not more than 20 mol. % A is $\frac{1}{2}\text{Dy}_2\text{O}_3$, not more than 20 mol. % A is $\frac{1}{2}\text{Sb}_2\text{O}_3$, not more than 35 mol. % A is PbO and not more than 25 mol. % A is

SnO, wherein B represents Al_2O_3 , wherein not more than 20 mol. % of the Al_2O_3 in B may be replaced by Sc_2O_3 , not more than 10 mol. % of the Al_2O_3 in B may be replaced by Cr_2O_3 and not more than 10 mol. % of the Al_2O_3 in B may be replaced by a chemically equivalent quantity of a combination of equimolar quantities of SiO_2 and (MgO and/or ZnO), wherein C represents at least one of the oxides MgO, ZnO, $\frac{1}{2}\text{LiAlO}_2$ and MnO, wherein not more than 20 mol. % of C consists of MnO, wherein up to 98 mol. % of A may be replaced by SrO and/or CaO when simultaneously or equimolar quantity of C is replaced by $\frac{1}{2}\text{Al}_2\text{O}_3$, where [A] is at least 0.02, [B] is at least 0.55 and is not more than 0.95, and [C] is at least $\frac{1}{2}[A]$, wherein $[A] + [B] + [C] = 1$.



1/4

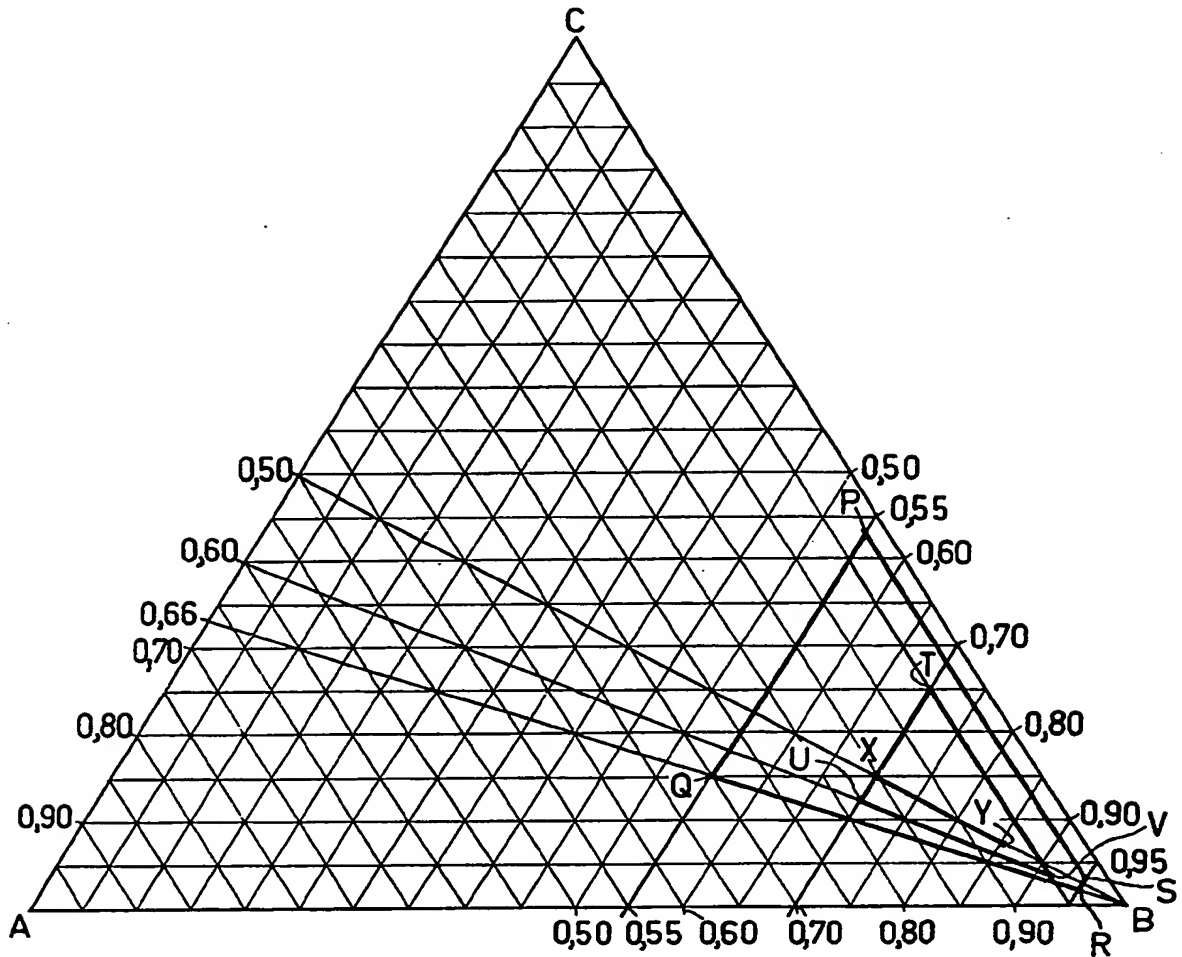


FIG.1

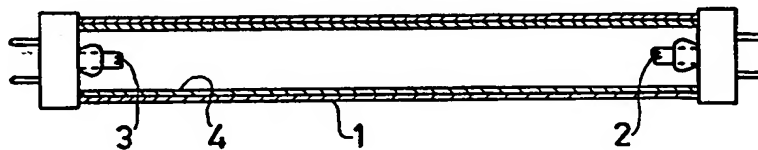


FIG.8

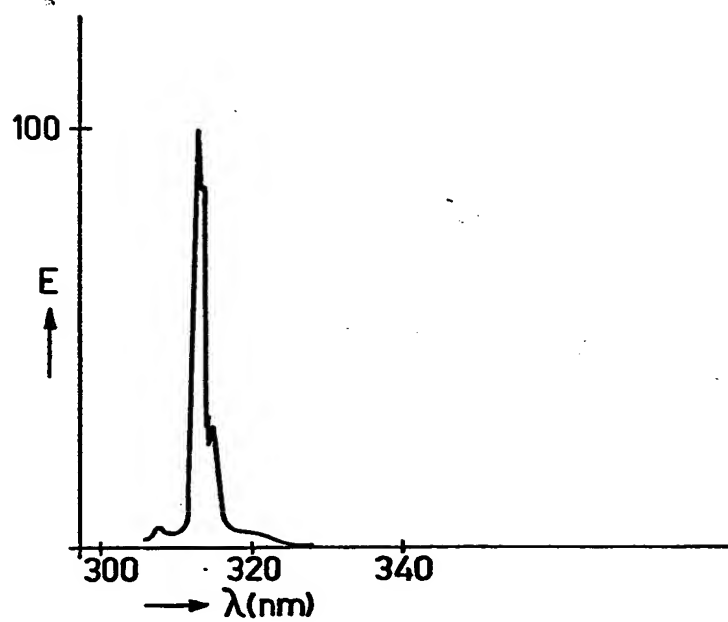


FIG.2

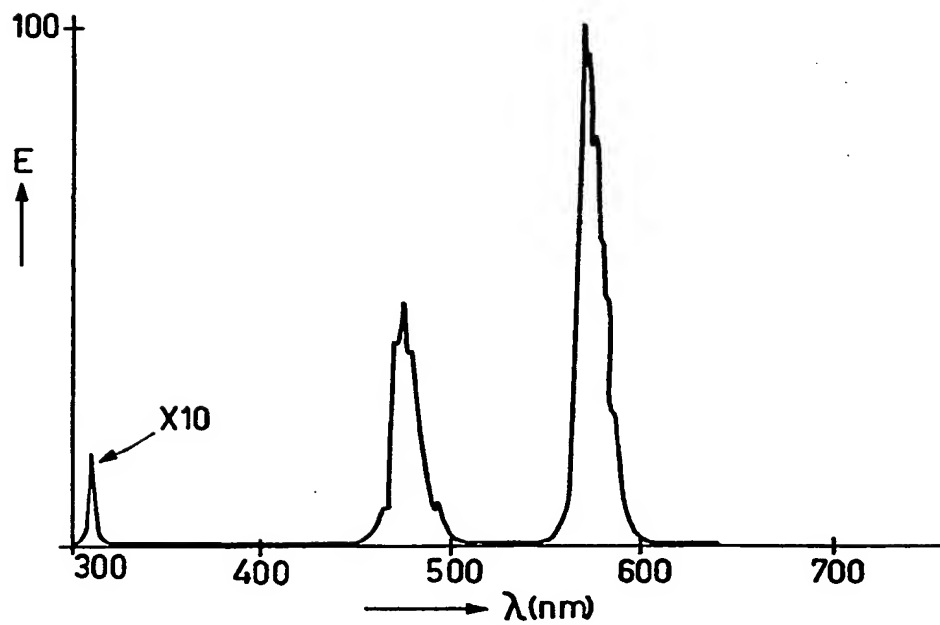


FIG.3

3/4

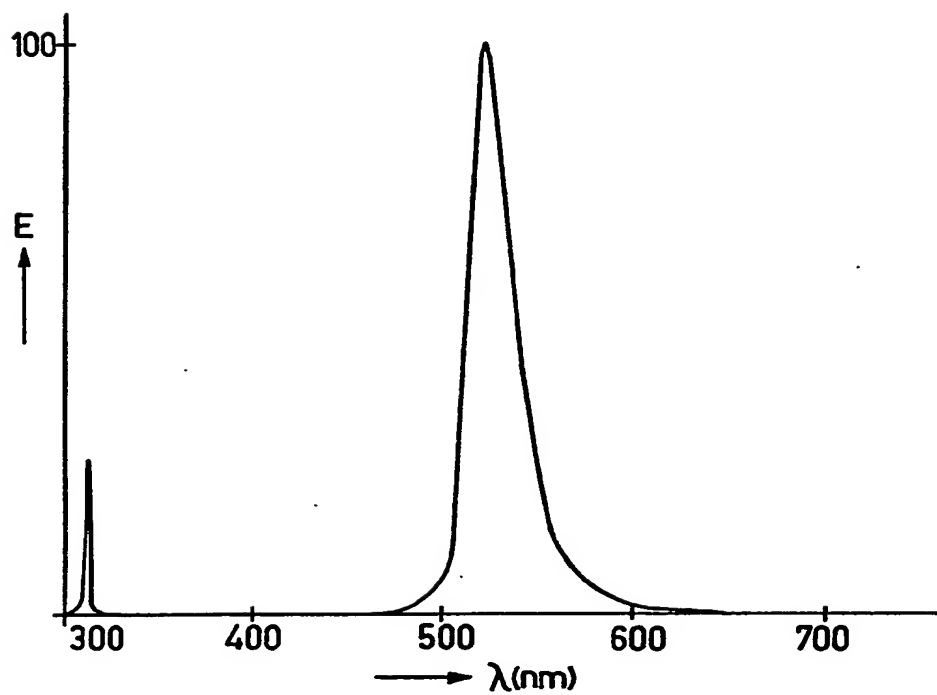


FIG.4

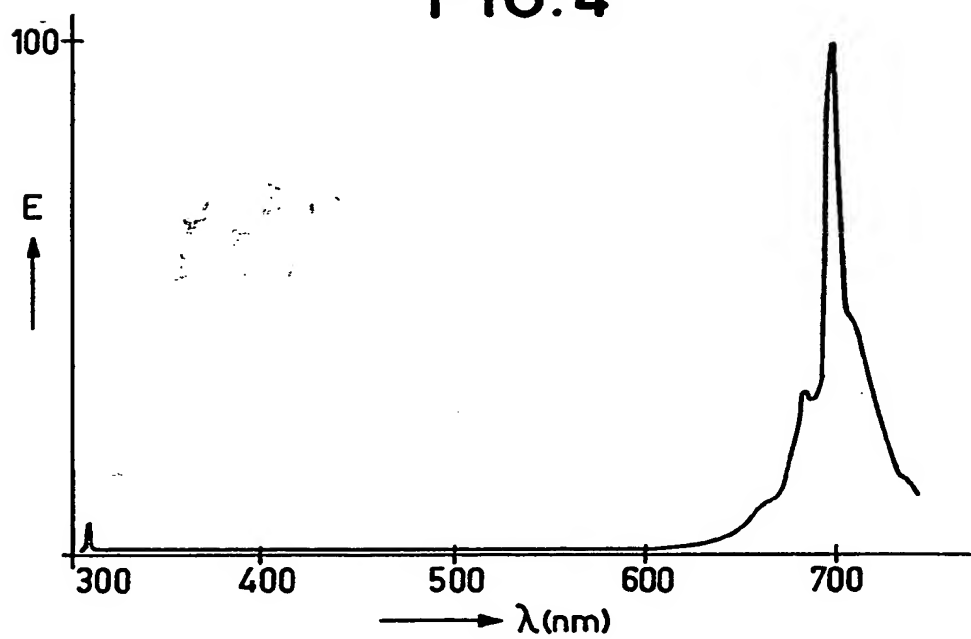


FIG.5

4/4

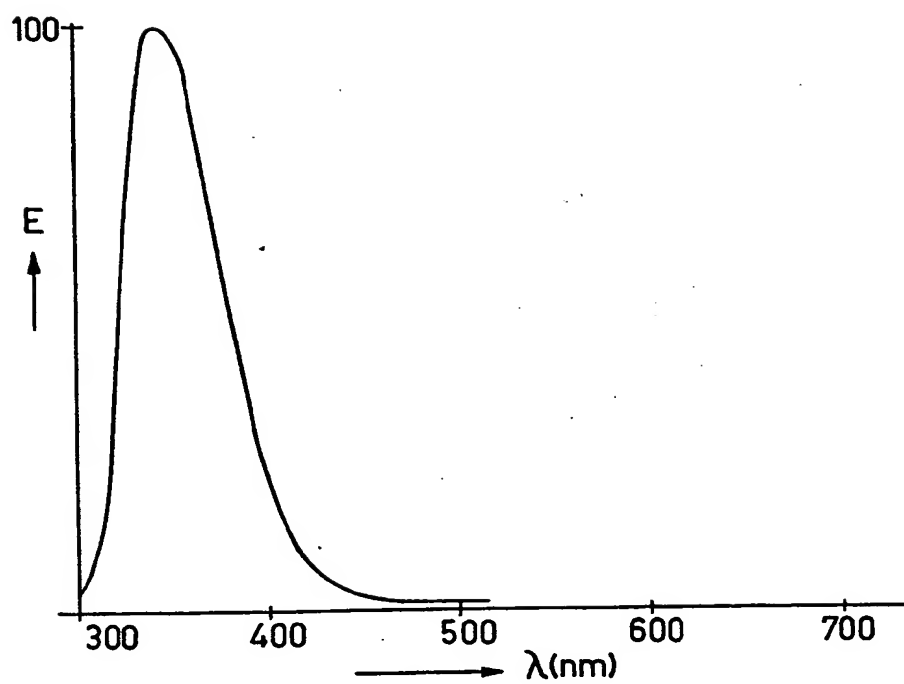


FIG. 6

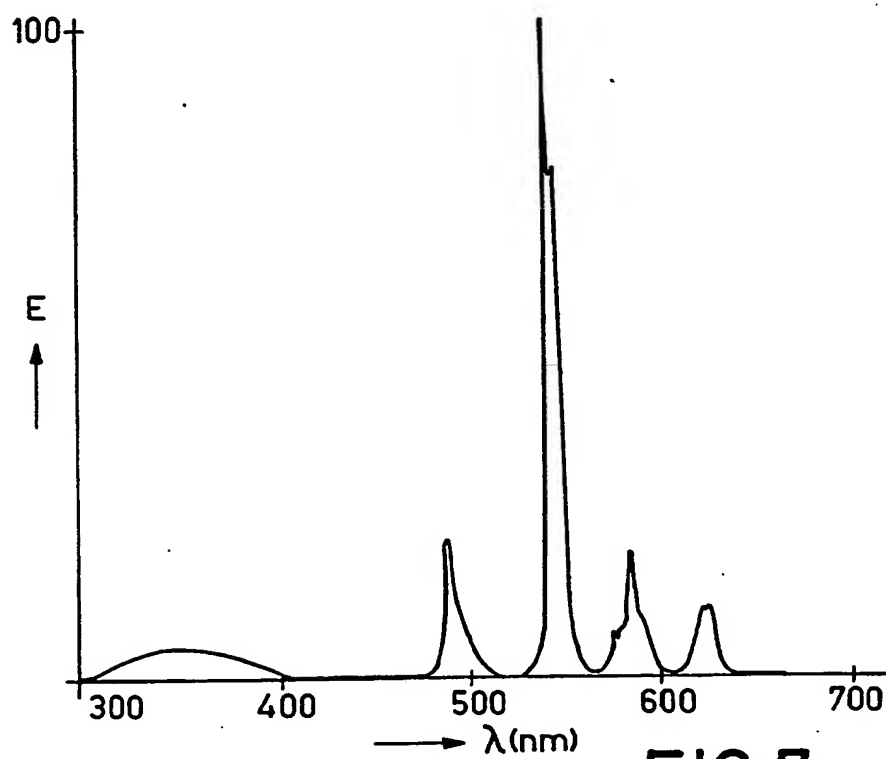


FIG. 7

SPECIFICATION

Luminescent Materials

5 The invention relates to a luminescent material comprising a luminescent ternary aluminate with a hexagonal crystal structure corresponding to the magnetoplumbite structure. In addition, the invention relates to a method of producing such an aluminate, to a luminescent screen comprising such an aluminate and to a low-pressure mercury vapour discharge lamp having such a luminescent screen.

Luminescent ternary aluminates are known from Netherlands Patent Application 7,214,862, and the corresponding United Kingdom Patent Specification 1,452,083. These aluminates are composed of at least three oxides; besides Al_2O_3 , they comprise at least one oxide having a large positive ion and at least one oxide having a small bivalent ion, such as MgO or ZnO . They have a crystal structure corresponding to that of magnetoplumbite ($\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$). If lanthanum oxide and/or cerium oxide is chosen for the oxide having a large positive ion, ternary aluminates having a so-called distorted magnetoplumbite structure (see, for example, Journal of Luminescence 14 (1976), pp 153-157) are obtained. The aluminates having this last-mentioned crystal structure are suitable host lattices for activation by, for example, terbium or dysprosium, whereby very efficiently luminescing materials can be obtained.

So far it had been assumed that the use of oxides of rare earth metals having a relative large ion radius, such as lanthanum oxide or cerium oxide, was necessary for the formation of ternary aluminate lattices having a distorted magnetoplumbite structure. The trivalent lanthanum and cerium ions have radii of 1.016 and 1.034 Å, respectively (see Handbook of Chemistry and Physics, Cleveland, Ohio).

It is an object of the invention to provide novel luminescent ternary aluminates having a crystal structure corresponding to that of magnetoplumbite.

The invention provides a luminescent material comprising a luminescent ternary aluminate having a hexagonal crystal structure corresponding to the magnetoplumbite structure, characterized in that the aluminate comprises gadolinium and is activated by at least one of the elements Pb, Sb, Ce, Sn, Tb, Mn, Cr, and Dy, the composition of the aluminate can be represented in a ternary phase diagram of a system ABC, wherein A represents $\frac{1}{2}\text{Gd}_2\text{O}_3$ and at least one of the oxides $\frac{1}{2}\text{La}_2\text{O}_3$, $\frac{1}{2}\text{Ce}_2\text{O}_3$, $\frac{1}{2}\text{Tb}_2\text{O}_3$, $\frac{1}{2}\text{Dy}_2\text{O}_3$, $\frac{1}{2}\text{Sb}_2\text{O}_3$, PbO, SnO, wherein at least 1 mol. % A is $\frac{1}{2}\text{Gd}_2\text{O}_3$, not more than 60 mol. % A is $\frac{1}{2}\text{Tb}_2\text{O}_3$, not more than 20 mol. % A is $\frac{1}{2}\text{Dy}_2\text{O}_3$, not more than 20 mol. % A is $\frac{1}{2}\text{Sb}_2\text{O}_3$, not more than 35 mol. % A is PbO and not more than 25 mol. % A is SnO, wherein B represents Al_2O_3 , wherein not more than 20 mol. % of the Al_2O_3 , wherein not more than 20 mol. % of the Al_2O_3 in B may be replaced by Sc_2O_3 , not more than 10 mol. % of the Al_2O_3 in B may be replaced by a chemically equivalent quantity of a combination of equimolar quantities of SiO_2 and (MgO and/or ZnO), wherein C represents at least one of the oxides MgO , ZnO , $\frac{1}{2}\text{LiAlO}_2$ and MnO , wherein not more than 20 mol. % of C consists of MnO , wherein up to 98 mol. % of A may be replaced by SrO and/or CaO when simultaneously on equimolar quantity of C is replaced by $\frac{1}{2}\text{Al}_2\text{O}_3$, wherein [A] is at least 0.02, [B] is at least 0.55 and is not more than 0.95, and [C] is at least $\frac{1}{2}$ [A], wherein $[A] + [B] + [C] = 1$.

During the investigations which led to the invention, it was found that ternary aluminates with distorted magnetoplumbite structure can be obtained with $\frac{1}{2}\text{Gd}_2\text{O}_3$ as the oxide having a large positive ion. This was unexpected as the radius of the trivalent Gd-ion (0.938 Å) is considerably smaller than that of La or Ce ions.

The luminescent ternary aluminates of the luminescent materials according to the invention are ternary compounds whose composition can be represented in the ternary phase diagram ABC, A representing the oxide having a large positive ion and C (when unsubstituted) being the oxide having a small bivalent ion. B represents the aluminium oxide.

It was found that the novel Gd-containing aluminates can form a complete series of mixed crystals having the same crystal structure, with the known La and/or Ce-containing aluminates. Therefore, in a luminescent aluminate according to the invention, not only $\frac{1}{2}\text{Gd}_2\text{O}_3$, but also $\frac{1}{2}\text{La}_2\text{O}_3$ and $\frac{1}{2}\text{Ce}_2\text{O}_3$ can be used for the oxide A, it being necessary, however, that at least 1 mol. % of the oxide A consists of $\frac{1}{2}\text{Gd}_2\text{O}_3$.

Efficiently luminescing materials can be obtained if the oxide A includes $\frac{1}{2}\text{Ce}_2\text{O}_3$. In addition, it appeared that activation by means of one or more of the elements Tb, Dy, Sb, Pb, and Sn results in luminescent materials. The oxides of these activator elements form part of the oxide A. An efficient luminescence can already occur if 0.1 mol. % of the oxide A consists of an oxide of one of the above-mentioned activator elements. There are certain limits to the maximum quantity of activator oxide to be used because the solubility of these oxides in the lattices of these luminescent ternary aluminates is limited and/or because in the case of excessive activator contents, materials are obtained whose luminescence is too low for practical purposes, owing to concentration quenching. Therefore the oxide A in an aluminate according to the invention consists of not more than 60 mol. % of $\frac{1}{2}\text{Tb}_2\text{O}_3$, not more than 20 mol. % of $\frac{1}{2}\text{Dy}_2\text{O}_3$, not more than 20 mol. % of $\frac{1}{2}\text{Sb}_2\text{O}_3$, not more than 35 mol. % of PbO and not more than 25 mol. % of SnO. Even if more than one of the above-mentioned activator oxides are used, at least 1 mol. % of A is $\frac{1}{2}\text{Gd}_2\text{O}_3$.

In luminescent ternary aluminate of luminescent materials according to the invention, up to 20 mol. % of the Al_2O_3 (denoted by B in the above-mentioned general formulation) may be replaced by Sc_2O_3 . Generally, such a substitution has little influence on the luminescent properties and does not furnish additional advantages. If more than 20 mol. % of Sc_2O_3 is used, materials are obtained whose luminous flux is too low and which are furthermore, expensive owing to the use of the expensive element scandium. It appeared that

the aluminates can be activated by chromium. The chromium oxide then replaces a portion of the Al_2O_3 . An efficient chromium emission can already occur if 0.1 mol. % of B consists of Cr_2O_3 . Not more than 10 mol. % of B is replaced by Cr_2O_3 , as with higher Cr contents the luminous fluxes obtained will be too low owing to concentration quenching.

- 5 Part of the oxide B may consist of gallium oxide, this also resulting in ternary compounds having a structure corresponding to magnetoplumbite. In general, the use of Ga_2O_3 for oxide B does not furnish advantages. Furthermore, the element gallium is more expensive than aluminium, so that gallium-free aluminates are preferably used. 5

- The oxide having a small bivalent ion C may be MgO , ZnO or $\frac{1}{2}\text{LiAlO}_2$. The aluminates can be activated by manganese and then MnO forms part of the oxide C. An efficient Mn-emission can already be produced if 0.1 mol. % of C consists of MnO . Not more than 20 mol. % of C is MnO used, because with such large quantities of Mn, luminous fluxes are obtained which are too small, again owing to concentration quenching. 10

- It appeared that in the luminescent aluminates of luminescent materials according to the invention, not more than 10 mol. % of the Al_2O_3 may be replaced by a chemically equivalent quantity of the combination of 15 equimolar quantities of SiO_2 and (MgO and/or ZnO) in accordance with: $p\text{Al}_2\text{O}_3 \rightarrow p\text{SiO}_2 + p\text{MgO}(\text{ZnO})$. With such a substitution, the crystal structure of the aluminate is retained and little influence on the luminescent properties is found. 15

- It further appeared from experiments that there is a high degree of mutual solubility between the novel Gd-containing ternary aluminates having a distorted magnetoplumbite structure and the known Sr and/or 20 Ca-containing aluminates having the magnetoplumbite structure. It is therefore possible to replace in the aluminates according to the invention up to 98 mol. % of A by SrO and/or CaO if simultaneously an equimolar quantity of the oxide C is replaced by $\frac{1}{2}\text{Al}_2\text{O}_3$ in accordance with: $q\text{A} + q\text{C} \rightarrow q\text{SrO}(\text{CaO}) + q \cdot \frac{1}{2}\text{Al}_2\text{O}_3$ (for example: $q \cdot \frac{1}{2}\text{Gd}_2\text{O}_3 + q\text{MgO} \rightarrow q\text{SrO}(\text{CaO}) + q \cdot \frac{1}{2}\text{Al}_2\text{O}_3$). The compounds then obtained have a magnetoplumbite or a distorted magnetoplumbite structure and, on activation, furnish efficient luminescent materials. Also in this substitution at least 1 mol. % of the total quantity of oxide A together with SrO and 25 CaO consists of $\frac{1}{2}\text{Gd}_2\text{O}_3$. 25

- The composition of the aluminates according to the invention is found in the ternary phase diagram ABC in the area limited by the $[\text{A}] \geq 0.02$, $0.55 \leq [\text{B}] \leq 0.95$ and $[\text{C}] \geq \frac{1}{2}[\text{A}]$. $[\text{A}]$, $[\text{B}]$ and $[\text{C}]$ represent the contents or molar fractions of the oxides A, B, and C, respectively, the system ABC, and $[\text{A}] + [\text{B}] + [\text{C}] = 1$. Figure 30 1 of the drawing shows the ternary phase diagram ABC. All ternary compounds are represented by a point within the triangle ABC. The aluminates of luminescent materials according to the invention have a composition which can each be represented by a point on or within the rectangle PQRS. 30

- Points on or within the triangle TUV of the phase diagram in Figure 1 represent luminescent aluminates of according to the invention having $[\text{A}]$ of at least 0.05, $[\text{B}]$ of at least 0.70 and a $[\text{C}]$ which is at least equal to 2/3 35 of the $[\text{A}]$. All those aluminates have very good luminescent properties. 35

The highest luminous fluxes are obtained with aluminates for which $[\text{A}]$ is substantially equal to $[\text{C}]$ i.e. $1.05[\text{C}] \geq 0.95[\text{C}]$, and $[\text{B}]$ is at least 0.70 and not more than 0.85. In the phase diagram of Figure 1 these compounds are found on or very near the line XY.

- In the aluminates of luminescent materials according to the invention, MgO and/or ZnO are preferably 40 used for the oxide C because they furnish the best results. 40

- One group of aluminates according to the invention is formed by the lead-activated compounds wherein 25 to 99 mol. % of the oxide A consists of $\frac{1}{2}\text{Gd}_2\text{O}_3$ and from 1 to 35 mol. % of the oxide A consists of PbO . These materials show in a very efficient manner the characteristic line emission of gadolinium at a wavelength of approximately 313 nm, the lead acting as the so-called sensitizer for the gadolinium emission. 45 These aluminates are very suitable for use in lamps, for example, low-pressure mercury vapour discharge lamps, for influencing photochemical processes, and in particular for medical irradiation purposes. These aluminates of luminescent materials according to the invention, which are the most efficient, by luminescing materials having a Gd-emission available so far, have the great advantage that when used in lamps they evidence only a small decay of the radiant flux during the life of the lamps. 50

- It should be noted that Gd emission can also be obtained by means of the Gd-containing aluminates activated by Sb. It appeared that the compounds sensitized with Sb are in general less efficient than the materials sensitized Pb. 50

- A further group of luminescent aluminates according to the invention is constituted by the materials wherein at least 25 mol. % of the oxide A consists of $\frac{1}{2}\text{Gd}_2\text{O}_3$ and which are activated by lead together with at least one of the elements Tb, Dy, Mn and Cr. These aluminates furnish in a very efficient manner the characteristic emission of Tb, Dy, Mn and Cr, respectively. In these materials the excitation energy is absorbed by the lead and thereafter transferred to the above-mentioned activators Tb, Dy, Mn and Cr via one or more Gd-ions. Particularly the Tb-activated aluminates of this further group have great advantages. On excitation by short wave ultra-violet radiation, for example, the 254 nm radiation of a low-pressure mercury vapour discharge, they have a quantum efficiency substantially corresponding to the most efficient materials with Tb-emission known so far. An advantage is that substantially no emission of lead of gadolinium is observed and that the aluminates, when used in lamps, evidence a very slight decay of the luminous flux over the life of the lamp. 60

- A third group of aluminates of luminescent materials according to the invention is constituted by the cerium-activated compounds. Hardly any concentration quenching occurs with this activation, so that from 1 65

to 99 mol. % of the oxide A may consist of $\frac{1}{2}\text{Ce}_2\text{O}_3$. The Ce-emission can be very efficient and consists of a band in the long-wave portion of the ultra-violet spectrum (maximum of the emission band, λ_{max} , depending on the composition of the aluminate, being at approximately 305 to 360 nm; half value width of the emission band, hvb being approximately 65 nm). These materials can be used advantageously in lamps for

5 influencing photochemical processes.

A fourth group of aluminates of luminescent materials according to the invention comprises, besides Ce, also at least one of the activator elements Tb, Dy, Mn, and Cr. In these compounds, transfer of the excitation energy is effected from the Ce, serving as a sensitizer, to the second activator, furnishing the characteristic emission of the second activator element.

10 On activator by bivalent tin, luminescent aluminates are obtained which have the tin emission when excited by, for example, 254 nm radiation. This emission is located in the near part of the ultra-violet spectrum (λ_{max} at 355-375 nm, hvb is approximately 60 nm).

It should be noted that transfer of excitation energy from tin to the above-mentioned elements Tb, Dy, Mn, and Cr is possible, but in general the tin-sensitized aluminates are less efficient than the above-described

15 Ce-sensitized compounds.

The luminescent aluminates of luminescent materials according to the invention are obtained by means of a solid state reaction at an elevated temperature of a mixture of starting materials. Preference is given to a method of preparing a luminescent aluminate, which is characterized in that a mixture is made of the oxides A, B, and C of the constituent elements of the aluminate to be formed and/or of compounds which on heating are converted into the relevant oxides, from 0.1 to 10 mol. % of the metal of oxide B and/or from 1 to 100 mol. % of the metal of oxide A and/or C being added to the mixture as a fluoride, and that the mixture is heated at 1200-1500°C. It appeared that the use of a fluoride of one of the constituent elements in the starting mixture greatly promotes the speed and completion of the formation reaction.

20 Preference is given to such a method, which is characterized in that from 0.1 to 10 mol. % of the aluminium in the mixture is used in the form of aluminium fluoride.

A further method according to the invention is characterized in that for each mole of aluminate to be formed, from 0.05 to 0.5 mole BaO and an excess of 0.3 to 3 mole Al_2O_3 , or compounds which on heating are converted into the relevant oxides, are added to the mixture. From experiments it appears that such an addition to the starting mixture results in luminescent aluminates having a higher luminous flux than when this addition is not effected. When adding BaO and an additional quantity of Al_2O_3 , barium aluminate is generally found in the reaction product besides the desired luminescent aluminate. This barium aluminate need not be removed as its quantity is only very small and it does not deleteriously affect the luminescent properties of the reaction product.

25 Some embodiments of the invention will now be described with reference to the following Examples and to the drawings, in which:-

Figure 1 shows the above-mentioned ternary phase diagram ABC,

Figure 2 shows the spectral energy distribution of the emission of a lead-activated aluminate,

Figure 3 shows the emission spectrum of an aluminate activated by lead and dysprosium,

Figure 4 shows the emission spectrum of an aluminate activated by lead and manganese.

40 *Figure 5* shows the emission spectrum of an aluminate activated by lead and chromium,

Figure 6 shows the emission spectrum of a cerium-activated aluminate,

Figure 7 shows the emission spectrum of an aluminate activated by cerium and terbium, and

Figure 8 is a schematic longitudinal section of a low-pressure mercury vapour discharge lamp according to the invention.

45 *Example 1.*

A mixture was made of

2.45 g Gd_2O_3

0.61 g MgO

50 8.26 g Al_2O_3

0.41 g $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$

0.50 g PbO

This mixture was heated in an oven for 2 hours in air at a temperature of 1450°C. After cooling and pulverizing it appeared that the product obtained consisted of a luminescent aluminate having a composition defined by the formula $\text{Gd}_{0.90}\text{Pb}_{0.15}\text{MgAl}_{11}\text{O}_{19}$. An X-ray diffraction analysis showed that the aluminate had the crystal structure of distorted magnetoplumbite. On excitation by radiation from a low-pressure mercury vapour discharge (predominantly 254 nm), the aluminate appeared to have the characteristic line emission of Gd. *Figure 2* shows the emission spectrum consisting of a very narrow band (half value width, hvb approximately 4 nm) having a maximum 313 nm. In *Figure 2*, the wavelength, λ , is plotted on the horizontal axis in nm and the relative intensity, E, of the emission in arbitrary units is plotted on the vertical axis. The absorption of the exciting ultra-violet radiation, A, was 93 % for the aluminate. The top value of the emission band, tv, appeared to be 69 % of the top value of the known bismuth-activated borate having a composition defined by the formula $\text{Gd}_{0.5}\text{La}_{0.487}\text{Bi}_{0.013}\text{B}_3\text{O}_6$, which also shows the Gd-emission.

Examples 2 to 17 inclusive.

In an analogous manner as described in Example 1, a number of lead-activated aluminates were prepared (Examples 2 to 15 inclusive) wherein the composition of the aluminate was varied. In addition, two antimony-activated aluminates (Examples 16 and 17) were prepared by using Sb_2O_3 in the firing mixture instead of PbO . Also these aluminates show efficient Gd-emissions. The results of measurements made on these materials are summarized in Table I. For each example the Table shows, in addition to the formula of the aluminate, the top value, tv, in a percentage figure relative to the above-mentioned, known borate, and further more, the absorption, A, of exciting radiation in %

TABLE I				
Example	Formula	tv	A	
1	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{MgAl}_{11}\text{O}_{19}$	69	93	
2	$\text{Gd}_{2.80}\text{Pb}_{0.30}\text{Mg}_6\text{Al}_{22}\text{O}_{43.50}$	41	81	
3	$\text{Gd}_{0.87}\text{Pb}_{0.20}\text{Mg}_6\text{Al}_{26}\text{O}_{46.505}$	57	74	
4	$\text{Gd}_{0.92}\text{Pb}_{0.12}\text{MgAl}_6\text{O}_{11.5}$	57	89	
5	$\text{Gd}_{0.87}\text{Pb}_{0.20}\text{Mg}_4\text{Al}_{30}\text{O}_{50.505}$	51	70	
6	$\text{Gd}_{0.87}\text{Pb}_{0.20}\text{MgAl}_{16}\text{O}_{26.505}$	66	86	
7	$\text{Gd}_{0.87}\text{Pb}_{0.20}\text{MgAl}_{36}\text{O}_{56.505}$	45	68	
8	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{MgAl}_{10.8}\text{Sc}_{0.2}\text{O}_{19}$	64	94	
9	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{MgAl}_{10}\text{ScO}_{19}$	49	87	
10	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{MgAl}_9\text{Sc}_2\text{O}_{19}$	34	75	
11	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{Mg}_{0.97}\text{Zn}_{0.03}\text{Al}_{11}\text{O}_{19}$	71	93	
12	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{Mg}_{0.80}\text{Zn}_{0.20}\text{Al}_{11}\text{O}_{19}$	68	93	
13	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{Mg}_{0.50}\text{Zn}_{0.50}\text{Al}_{11}\text{O}_{19}$	64	93	
14	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{Mg}_{0.20}\text{Zn}_{0.80}\text{Al}_{11}\text{O}_{19}$	60	93	
15	$\text{Gd}_{0.90}\text{Pb}_{0.15}\text{ZnAl}_{11}\text{O}_{19}$	58	93	
16	$\text{Gd}_{0.9}\text{Sb}_{0.1}\text{MgAl}_{11}\text{O}_{19}$	33	65	
17	$\text{Gd}_{0.85}\text{Sb}_{0.15}\text{MgAl}_{11}\text{O}_{19}$	33	67	

Example 18.

A lead-activated aluminate was prepared in an analogous manner to that described in Example 1. However, for each mole of the aluminate to be formed 0.25 mole BaCO_3 and 1.50 mole Al_2O_3 were added to the firing mixture. To this end a mixture was made of

- 1.27 g Gd_2O_3
 - 0.40 g BaCO_3
 - 0.32 g MgO
 - 5.66 g Al_2O_3
 - 0.14 g $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$
 - 0.34 g PbO
- The mixture was heated for 2 hours at 1450°C in air. The product obtained was an aluminate having a composition defined by the formula $\text{Gd}_{0.875}\text{Pb}_{0.1875}\text{MgAl}_{11}\text{O}_{19}$ and appeared to have the crystal structure of distorted magnetoplumbite. The aluminate contained a small quantity of barium aluminate which did not impair the luminescent properties of the luminescent material.

Example 19

The same procedure as described in Example 18 was followed. However, the firing mixture now contained ZnO instead of MgO .

Examples 20 to 22 inclusive.

- By means of the methods described for the preceding Examples, three lead-activated aluminates were obtained wherein a portion of the aluminium oxide was replaced by an equivalent quantity of a combination consisting of equimolar quantities of SiO_2 and MgO .

The following Table II shows the formulae of the aluminates and the results of the top value measurement and absorption for Examples 18 to 22 inclusive.

TABLE II

Example	Formula	tv	A	
18 ¹⁾	Gd _{0.875} Pb _{0.1875} MgAl ₁₁ O ₁₉	70	81	
5 19 ¹⁾	Gd _{0.875} Pb _{0.1875} ZnAl ₁₁ O ₁₉	74	81	5
20 ²⁾	Gd _{0.90} Pb _{0.10} Mg _{1.5} Al ₁₀ Si _{0.5} O _{18.95}	60	85	
21 ³⁾	Gd _{0.875} Pb _{0.125} Mg _{1.25} Al _{10.50} Si _{0.25} O _{18.94}	64	77	
10 22 ⁴⁾	Gd _{60.875} Pb _{0.125} Mg _{1.25} Al _{10.50} Si _{0.25} O _{18.94}	73	75	10
1) 0.25 mole BaCO ₃ and 1.5 mole Al ₂ O ₃ for each mole of the aluminate to be formed were added to the firing mixture.				
2) The firing mixture was heated 1500°C.				
3) 0.25 mole BaCO ₃ and 1.375 mole Al ₂ O ₃ were added. The firing mixture was heated at 1400°C.				
15 4) 0.25 mole BaCO ₃ and 1.44 mole Al ₂ O ₃ were added. The firing mixture was heated at 1500°C. The quantum efficiency of the material of Example 22 was 55%.	15			

Examples 23 to 27 inclusive.

20	Five aluminates, activated by lead and terbium, were obtained by heating a starting mixture in a nitrogen atmosphere at 1400°C (Examples 23 to 25 inclusive) or at 1500°C (Examples 26 and 27). Table III shows the formulae of the materials. In addition, the Table specifies for these aluminates the quantum efficiency, q , as a percentage on excitation by 254 nm radiation and the absorption, A , of the exciting radiation (in %). In these materials the excitation energy is absorbed in the lead and transferred to the terbium activator <i>via</i> one or more Gd ions. The materials show an efficient terbium emission, substantially no lead and gadolinium emission being observed.				20
25					25

TABLE III

30	Example	Formula	<i>q</i>	A	30
	23	Gd _{0.8} Tb _{0.1} Pb _{0.1} Mg _{0.9} Al _{11.1} O ₉	51	85	
	24	Gd _{0.85} Tb _{0.1} Pb _{0.05} Mg _{0.95} Al _{11.05} O ₁₉	56	72	
35	25 ¹⁾	Gd _{0.67} Tb _{0.22} Pb _{0.11} Mg _{1.12} Al _{10.95} O _{18.99}	81	73	35
	26 ²⁾	Gd _{0.58} Tb _{0.21} Pb _{0.21} Mg _{1.06} Al ₁₁ O _{18.955}	75	82	
	27 ²⁾	Gd _{0.48} Tb _{0.26} Pb _{0.26} Mg _{1.06} Al ₁₁ O _{18.93}	76	85	
40	1) 0.10 mole BaCO ₃ and 0.60 mole Al ₂ O ₃ were added to the firing mixture.				40
	2) 0.05 mole BaCO ₃ and 0.30 mole Al ₂ O ₃ were added to the firing mixture.				

Examples 28 to 31 inclusive.

45	An efficient transfer of excitation energy <i>via</i> Gd-ions to Dy, Mn or Cr is also possible in the lead-activated aluminates. Table IV shows the formulae of four examples of such aluminates. In addition, the table states the value of the quantum efficiency, q , and the absorption A .				45
----	---	--	--	--	----

TABLE IV

50	Example	Formula	q	A	50
	28	$Gd_{0.80}Dy_{0.10}Pb_{0.15}ZnAl_{11}O_{19}$	37	89	
	29 ¹⁾	$Gd_{0.80}Dy_{0.10}Pb_{0.15}MgAl_{11}O_{19}$	28	87	
55	30 ²⁾	$Gd_{0.875}Pb_{0.125}Mg_{1.125}Mn_{0.125}Al_{10.50}Si_{0.25}O_{18.94}$	31	82	55
	31 ³⁾	$Gd_{0.90}Pb_{0.15}MgAl_{11.49}Cr_{0.01}O_{19.75}$	30	91	
60	1) Figure 3 shows the spectral energy distribution of the radiation emitted by this material at 254 nm excitation. The emission spectrum consists of the characteristic Dy-bands at approximately 480 and 575 nm. In addition, the Gd-line emission is found at 313nm (shown in Figure 3 at a 10x reduced scale).				60
	2) 0.25 mole BaCO ₃ and 1.44 mole Al ₂ O ₃ were added to the firing mixture. Figure 4 shows the emission spectrum of this aluminate, which spectrum appears to consist of the green manganese band, the maximum being at approximately 525 nm. Also here the Gd-emission is still observable.				
65					65

3) Figure 5 shows the emission spectrum of this material. It consists of a narrow band, the maximum being at approximately 700 nm.

Example 32

- 5 A mixture was made of 5
- 1.61 g Gd_2O_3
- 0.51 g MgO
- 7.05 g Al_2O_3
- 0.17 g $AlF_3 \cdot 3H_2O$
- 10 0.65 g CeO_2 . 10
- This mixture was heated for 2 hours at $1450^\circ C$ in an oven through which nitrogen was passed (5 l/minute). After cooling and pulverizing a luminescent aluminate was obtained having a composition defined by the formula $Gd_{0.70}Ce_{0.30}MgAl_{11}O_{19}$. On 254 nm excitation the material shows the Ce-emission (a band in the near portion of the UV-spectrum with a maximum at approximately 340 nm). Figure 6 shows the emission spectrum. The relative to a luminescent material used as a standard. This standard was the known lead-activated barium disilicate which emits in the same portion of the spectrum. The absorption, A, of the exciting radiation was 93%.
- 15 15

Examples 33 to 47 inclusive.

- 20 In an analogous manner as described in Example 32, a number of cerium-activated aluminates having different compositions were made. Table V shows the formulae of these materials (Examples 33 to 45 inclusive), as well as the results of the measurement of the relative intensity, I, in a percentage figure with respect to the standard mentioned in Example 32 and of the absorption, A, of the exciting radiation. Examples 46 and 47 relate to tin-activated aluminates. These materials emit in a band ($h\nu = 60$ nm) with a maximum at approximately 375 nm.
- 25 25

TABLE V

30 Example	Formula	I	A	30
32	$Gd_{0.70}Ce_{0.30}MgAl_{11}O_{19}$	93	93	
33	$Gd_{0.99}Ce_{0.01}MgAl_{11}O_{19}$	44	57	
35 34	$Gd_{0.90}Ce_{0.10}MgAl_{11}O_{19}$	86	89	35
35	$Gd_{0.50}Ce_{0.50}MgAl_{11}O_{19}$	86	95	
36	$Gd_{0.25}Ce_{0.75}MgAl_{11}O_{19}$	73	96	
37	$Gd_{0.01}Ce_{0.99}MgAl_{11}O_{19}$	85	97	
40 38	$La_{0.2}Gd_{0.5}Ce_{0.3}MgAl_{11}O_{19}$	85	94	40
39	$La_{0.5}Gd_{0.2}Ce_{0.3}MgAl_{11}O_{19}$	85	93	
40	$La_{0.2}Gd_{0.5}Ce_{0.3}ZnAl_{11}O_{19}$	80	94	
45 41	$La_{0.5}Gd_{0.2}Ce_{0.3}ZnAl_{11}O_{19}$	85	93	45
42	$Gd_{0.9}Ce_{0.1}ZnAl_{11}O_{19}$	78	91	
43	$Gd_{0.7}Ce_{0.3}ZnAl_{11}O_{19}$	65	96	
50 44	$Gd_{0.10}Sr_{0.85}Ce_{0.05}Mg_{0.15}Al_{11.85}O_{19}$	1)	-	50
45	$Gd_{0.50}Sr_{0.45}Ce_{0.05}Mg_{0.55}Al_{11.45}O_{19}$	2)	-	
46	$GdSn_{0.1}MgAl_{11}O_{19.1}$	38	60	
55 47	$GdSn_{0.1}ZnAl_{11}O_{19.1}$	41	55	55

1) Quantum efficiency at 254 nm-excitation: 77% $\lambda_{max} = 310$ nm

2) Quantum efficiency at 254 nm-excitation: 55% $\lambda_{max} = 340$ nm

Examples 48 to 54 inclusive

- 60 In an analogous manner as described in Example 32 Ce-activated aluminates were made which also comprises Tb, Dy and Cr as the activator. These materials showed the radiation characteristic of the last-mentioned activators. Table VI states the formula, the quantum efficiency, q, and the absorption, A, for each of these materials.
- 60

Example	Formula	q	A	
48	$Gd_{0.52}Ce_{0.15}Tb_{0.33}MgAl_{11}O_{19}$	73	91	
5 49 ¹⁾	$Gd_{0.37}Ce_{0.30}Tb_{0.33}MgAl_{11}O_{19}$	74	95	5
50	$Gd_{0.22}Ce_{0.45}Tb_{0.33}MgAl_{11}O_{19}$	76	96	
51	$Gd_{0.01}Ce_{0.66}Tb_{0.33}MgAl_{11}O_{19}$	77	96	
52	$Gd_{0.37}Ce_{0.30}Tb_{0.33}ZnAl_{11}O_{19}$	63	96	
10 53	$Gd_{0.60}Ce_{0.30}Dy_{0.10}ZnAl_{11}O_{19}$	17	94	10
54	$Gd_{0.65}Ce_{0.30}MgAl_{11}Cr_{0.05}O_{19}$	20	-	

- 1) Figure 7 shows the emission spectrum of this material. In addition to the characteristic Tb-emission a small contribution of the Ce-band to the emitted radiation is still observable. 15
- Figure 8 of the drawing is a schematic longitudinal section of a low-pressure mercury vapour discharge lamp according to the invention. The lamp comprises a tubular glass envelope 1. At the ends of the lamp electrodes 2 and 3 are disposed, one at each end, between which the discharge takes place during operation. The lamp contains a mixture of rare gases, serving as the starting gas, and a small quantity of mercury. The envelope 1 serves as the substrate for a luminescent layer 4, which comprises a luminescent aluminate according to the invention. The layer 4 can be provided in a customary manner to the envelope, for example, by means of a suspension containing the luminescent aluminate. 20

CLAIMS

1. A luminescent material comprising a luminescent ternary aluminate having a hexagonal crystal structures corresponding to the magnetoplumbite structure, characterized in that the aluminate comprises gadolinium and is activated by at least one of the elements Pb, Sb, Ce, Sn, Tb, Mn, Cr, and Dy, the composition of the aluminate can be represented in a ternary phase diagram of a system ABC, wherein A represents $\frac{1}{2}Gd_2O_3$ and at least one of the oxides $\frac{1}{2}La_2O_3$, $\frac{1}{2}Ce_2O_3$, $\frac{1}{2}Tb_2O_3$, $\frac{1}{2}Dy_2O_3$, $\frac{1}{2}Sb_2O_3$, PbO, SnO, wherein at least 1 mol. % A is $\frac{1}{2}Gd_2O_3$, not more than 60 mol. % A is $\frac{1}{2}Tb_2O_3$, not more than 20 mol. % A is $\frac{1}{2}Dy_2O_3$, not more than 20 mol. % A is $\frac{1}{2}Sb_2O_3$, not more than 35 mol. % A is PbO and not more than 25 mol. % A is SnO, wherein B represents Al_2O_3 , wherein not more than 20 mol. % of the Al_2O_3 in B may be replaced by Sc_2O_3 , not more than 10 mol. % of the Al_2O_3 in B may be replaced by Cr_2O_3 and not more than 10 mol. % of the Al_2O_3 in B may be replaced by a chemically equivalent quantity of a combination of equimolar quantities of SiO_2 and (MgO and/or ZnO), wherein C represents at least one of the oxides MgO, ZnO, $\frac{1}{2}LiAlO_2$ and MnO, wherein not more than 20 mol. % of C consists of MnO, wherein up to 98 mol. % of A may be replaced by SrO and/or CaO when simultaneously an equimolar quantity of C is replaced by $\frac{1}{2}Al_2O_3$, wherein [A] is at least 0.02, [B] is at least 0.55 and is not more than 0.95, and [C] is at least $\frac{1}{2}[A]$, wherein $[A] + [B] + [C] = 1$. 30
2. A luminescent material as claimed in Claim 1, characterized in that [A] is at least 0.05, [B] is at least 0.70, and [C] is at least equal to $\frac{2}{3}$ of [A]. 35
3. A luminescent material as claimed in Claim 2, characterized in that $1.05[C] \geq [A] \geq 0.95[C]$ and that the content of [B] is at least 0.70 and not more than 0.85. 40
4. A luminescent material as claimed in any of Claims 1 to 3, characterized in that the aluminate is activated by lead from 1 to 35 mol. % of A being PbO and from 25 to 99 mol. % of A being $\frac{1}{2}Gd_2O_3$. 45
5. A luminescent material as claimed in Claim 4, characterized in that the aluminate is furthermore activated by at least one of the elements Tb, Dy, Mn, and Cr. 50
6. A luminescent material as claimed in any of Claims 1 to 3, characterized in that the aluminate is activated by cerium, from 1 to 99 mol. % A being $\frac{1}{2}Ce_2O_3$.
7. A luminescent material as claimed in Claim 6, characterized in that the aluminate is furthermore activated by at least one of the elements Tb, Dy, Mn, and Cr.
8. A luminescent material comprising a luminescent ternary aluminate, substantially as herein described with reference to any of Examples 1 to 54. 55
9. A method of preparing a luminescent material as claimed in any of Claims 1 to 7, characterized in that a mixture is made of the oxides A, B and C of the constituent elements of the aluminate to be formed and/or of compounds which on heating are converted into these oxides, from 0.1 to 10 mol. % of the metal of oxide B and/or from 1 to 100 mol. % of the metal of oxide A and/or C being added to the mixture as fluoride, and heating the mixture at 1200°C-1500°C. 60
10. A method as claimed in Claim 9, characterized in that from 0.1 to 10 mol. % of the aluminium is added to the mixture as aluminium fluoride.
11. A method as claimed in Claims 9 or 10, characterized in that there is furthermore added to the mixture for each mole of aluminate to be formed from 0.05 to 0.5 mole BaO and an excess of 0.3 to 3 mol Al_2O_3 , or 65

compounds which on heating are converted into these oxides.

12. A luminescent screen comprising a substrate bearing a luminescent material as claimed in any of Claims 1 to 8.

13. A low-pressure mercury vapour discharge lamp a luminescent screen as claimed in Claim 12.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon Surrey, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.